

CRYSTALLINE POROUS SOLIDS, PRODUCTION AND USE THEREOF

Description

- 5 The invention relates to crystalline porous solids, to a method of producing them and to the use of them.

10 Porous solids have attracted increasing interest in years past. They combine the characteristics of a massive solid, such as mechanical strength, with certain application-specific advantages such as e.g. reduced weight, high surface area, in some cases permeability to relatively small molecules or exclusion of relatively large molecules etc. Important fields of application for the porous materials are therefore found in separation technology or catalysis.

15 Previously known porous solids consist of ceramic materials having low conductivity and are produced via precursor methods or decomposition methods. They are therefore of no use or of only limited use as conductive materials (e.g. in sensor technology).

20 Such a method of producing porous solids having low conductivity is described e.g. in DE 41 02 430 A1. According to DE 41 02 430 A1, a fine-pored solid having a high pore volume is produced by a coarsely disperse sedimentable mixture of a liquid phase and solid particles being caused to sediment and the sediment being solidified in the presence of the liquid phase by a chemical reaction between the sediment particles to form a porous body.

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30 DE 37 31 649 A1 describes a method of producing open-pored sintered bodies which comprises sintering a sinterable glass powder and an inorganic, soluble salt of defined granularity, whose melting point is above the melting temperature of the sinterable powder, and dissolving away, after cooling, the soluble salt

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present in the sintered body. The glass powder used according to DE 37 31 649 A1 is distinguished, in particular, by high sinterability. This method too affords open-pored sintered bodies which consist of glass ceramics and have low conductivity.

There is therefore a need for porous materials having a conductivity which is higher than that of the known porous ceramics.

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The present invention therefore relates to a method of producing a porous solid, characterized by the steps of:

- (i) preparing a fluid mixture comprising a first phase which includes one or more inorganic ionic components, and at least one second phase, the first phase and the second phase being essentially immiscible in the solid state,
- (ii) cooling the fluid mixture to a temperature below the solidification point in order to form a solid phase mixture comprising at least one first crystalline phase and a second phase, and
- (iii) removing the second phase.

The advantages of the method described here consist in the simplicity of the production of porous conductive solids, which involves the preparation of a preferably eutectic mixture of at least two solid phases, at least one soluble and one insoluble phase. The morphology of the phases can be influenced by simple variation of the preparation conditions or of the quenching rate. Removal of the soluble phase results in the formation of an open pore network. Thus, porous conductive, especially ion-conducting, electroceramics are accessible which owing to the microstructure of the eutectic have high mechanical stability. The significance of the method inter alia resides in the fact that - as shown in the examples - the highly

porous materials obtained provide a large contact area and are therefore of importance for the use in sensorics, e.g. in gas sensorics. Equally, the solids according to the invention can also serve as containers
5 for a liquid electrolyte. Owing to interface interactions, the solid can be filled in a simple manner with electrolyte liquid and subsequent bleeding of the latter (phase separation) can be prevented.

10 The porous solid resulting from the method has an essentially open-pored structure and, owing to its crystalline composition has a high conductivity, especially ionic conductivity. The mean pore size depends on the structure of the phase which has been
15 dissolved away and can therefore vary over a wide range. Thus, the pores can e.g. have a size in the order of from about 20 nm to 5 μm in each spatial direction. Anisotropic pore structure can likewise be obtained, e.g. lamellar pore structures, which can have
20 pore sizes of from 2 to 3.5 $\mu\text{m} \times 500 \text{ nm}$ up to 1.5 $\mu\text{m} \times 20 \text{ nm}$ to 200 nm. The degree of the porosity (fraction of the pore volume relative to the total volume) depends on the respective fractions of the first and second phases in the fluid mixture and can
25 range from about 10 to 70%, preferably from 20 to 50%.

The fluid mixture prepared in step (i) of the method according to the invention includes at least two phases, which are miscible in the fluid state but not
30 in the solid state. The term "fluid state" refers to a melt or alternatively e.g. a plasma. The first phase includes one or more inorganic ionic components, especially ionic compounds such as salts, for example. Preferred examples of such compounds are
35 water-insoluble salts, e.g. silver halides, especially AgCl.

The second phase comprises a substance which in the solid state is immiscible with the first phase and preferably is essential miscible therewith in the fluid state. Preferably, the second phase used is a
5 water-soluble salt compound which is able to form a eutectic mixture with the first phase. If the first phase is a silver halide, e.g. AgCl, the second phase used can be an alkaline earth metal halide or alkali metal halide, e.g. KCl, RbCl or/and CsCl. Particularly
10 preferred is a eutectic mixture comprising about 70 mol% of AgCl and 30 mol% of KCl.

According to step (ii) the fluid mixture is cooled to a temperature below the solidification point. This
15 affords a solid which contains a phase mixture comprising at least one first crystalline phase and a second, selectively removable phase. It is also possible for further phases to be present, which can be selectively removable soluble phases or/and insoluble
20 phases which remain in the resulting porous solid.

Via the cooling rate it is possible to vary the morphology of the resulting solid. According to one embodiment, cooling takes place under non-segregating
25 conditions (quenching), the cooling rate being sufficiently high to prevent crystal growth and consequently the formation of substantial crystals. In this case, the cooling rate is preferably in the range of from 10 to 50°C/min and above. In other cases,
30 slower cooling is also possible, to enable crystal growth to the extent desired. Thus, slow cooling of a non-eutectic fluid mixture first results in a fluid eutectic composition containing particles of the first or second phase dispersed therein, which then
35 solidifies as the temperature drops below the eutectic temperature. It is thus possible to produce a porous solid which includes two or more pore species which differ in terms of size or/and morphology.

Preferably, the fluid mixture has an essentially eutectic phase composition. Upon cooling of such a mixture, porous solids having a lamellar morphology can be obtained. The composition of the mixture is preferably in the range of ± 10 mol%, especially ± 2.5 mol% of a eutectic mixture.

The removal of the second phase from the solid can be effected, for example, by solvent extraction, if the first phase is insoluble in a particular solvent and the second phase is soluble therein. Preferentially, a second substance is used which is soluble in aqueous media (water, aqueous acid or bases). Where appropriate, however, organic solvents can also be used for the extraction.

As an alternative to a solvent extraction, the second phase can also be removed by other methods (chemical reactions or/and heating).

The invention further relates to a porous ion-conducting solid obtainable via the inventive method.

The porous solid can be employed directly for further use. Alternatively, however, it can also be ground down into smaller particles and be converted into a different shape, e.g. by compression molding. If the solid consists of an ion-conducting material it can be used in an electrochemical cell as an electrolyte, e.g. as a solid electrolyte or as a support for a liquid electrolyte. The electrochemical cell customarily contains at least two electrodes (e.g. measuring electrode and reference electrode) and the electrolyte disposed between the electrodes. The cell can be used as a sensor, e.g. as an amperometric or conductometric sensor for determining physical parameters, e.g. temperature, or chemical parameters, e.g. gaseous

substances such as H_2O , CO_2 and NH_3 . By using the inventive porous solids as electrolytes, a considerable increase in the sensitivity of such sensors is possible. A porous AgCl solid is suitable, in particular, for the determination of NH_3 .

The porous solid is also suitable for other applications (fluid supports, separation techniques, catalysis). For these purposes, the pores of the solid can, if required, be coated with further substances, e.g. metals, metal oxides or even biomolecules.

The invention is explained in more details by the following examples, in conjunction with the appended figures in which:

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Figure 1a is a scanning electron micrograph of the lamellar structure which was obtained by cooling a fluid mixture of a eutectic composition of AgCl and KCl (30 mol% KCl, 70 mol% AgCl),

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Figure 1b is a scanning electron micrograph of the porous AgCl solid obtained after the KCl phase had been dissolved away,

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Figure 2a is a diagram which shows the reversible change in the conductivity in a porous AgCl solid upon switching from an Ar atmosphere to an NH_3 atmosphere and back, and

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Figure 2b shows the change in the conductivity in a porous AgCl solid in the absence and the presence of a liquid electrolyte (0.5 M and 1 M AgNO_3) as a function of the temperature.

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Examples

1. Production of a porous AgCl solid

AgCl (70 mol%) and KCl (30 mol%) are heated to 350°C in a preheated furnace. The homogeneous melt is cooled to room temperature by being removed from the furnace.

5 Then the KCl is dissolved away by immersion in distilled water, and the resulting solid is dried in air for 24 h. A porous, mechanically stable solid is obtained. The porosity corresponds to the KCl content.

10 The structure of the solid before and after the extraction of KCl is shown in figures 1a and 1b.

2. Determination of NH_3

15 The porous AgCl solid according to example 1 is ground to a powder which is then compression-molded by uniaxial compression, using a pressure of about 30 kN/cm², to produce pellets having a diameter of 1 cm.

20 A pellet is arranged between two electrodes to produce an NH_3 sensor. Silver paste is used for the electrodes.

Figure 2a shows the change in conductivity of the porous AgCl specimen in the presence of NH_3 and inert gas (argon), respectively. A reproducible and reversible rapid change in conductivity proportional to the NH_3 concentration is observed.

30 3. Liquid-electrolyte support

A porous AgCl solid produced in accordance with example 1 is filled with liquid electrolyte (AgNO_3). Owing to the capillary forces, the liquid electrolyte is readily absorbed by the porous solid and retained therein.

35 Figure 2b shows the change in the conductivity of a porous AgCl solid in the presence and absence of AgNO_3 (0.5 M and 1 M) as a function of the temperature. As

can be gathered from the diagram, the porous AgCl solid is eminently suitable as a support for liquid electrolytes.